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XI.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE

ON THE DIRECT CONVERSION OF AROMATIC SULPHONATES INTO THE CORRESPONDING AMIDO COMPOUNDS.

By C. Loring Jackson and John F. Wing.

The action of sodium or potassium amide on organic substances has been studied but little; in fact, when we took up the subject, there were no papers more recent than those of Beilstein and Geuther * on sodium amide in 1858, and of Baumert and Landolt † on potassium amide in 1859. The reason for this neglect may be found probably in the curious observation made in both of these papers, that the alkaline amides are not acted on in the way which we should expect by most haloid organic compounds, neither ethylchloride, or iodide, nor chlorbenzol, nor acetylchloride giving the corresponding amido compounds; ‡ in fact, benzoylchloride is the only haloid organic compound tried which acted as would be expected, giving benzamide and dibenzamide. Accordingly, in taking up the subject, we have turned our attention to the effect of sodium amide on sulphonates, in the hope of obtaining an action similar to the well-known replacements of the sulpho-group by hydroxyl, cyanogen, or carboxyl, when fused with potassic hydrate, cyanide, or formiate respectively. This expectation

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* Ann. Chem., cviii. 88.

† Ibid., cxi. 1.

‡ These results so far as the ethyl compounds are concerned have been confirmed recently by J. Walter, who, in a paper (Journ. pr. Chem., xxxiv. 132) drawn out by the preliminary notice of our work, states that at low temperatures no ethylamine is formed from ethylbromide; but by heating the sodium amide until it begins to melt, and passing over it a stream of hydrogen impregnated with ethylbromide, ethylamine was formed, recognized by the carbylamine reaction. Under similar conditions brombenzol gave small quantities of aniline. He however does not consider it proved, that the amine was formed from the sodium amide, rather than from the ammonia set free during the reaction.

has been fulfilled, as by heating potassic benzolmonosulphonate with sodium amide we have obtained aniline, and in the same way metaphenylenediamine from potassic benzolmetadisulphonate; but unfortunately the yield, especially in the latter case, is so small, that the method could hardly be used with profit for the preparation of new amido compounds, so that its usefulness must be confined to determinations of constitution.

The sodium amide was prepared according to the method of Beilstein and Geuther, that is, passing dry ammonia gas over sodium heated in a series of small flasks, except that after the first experiment we dispensed with the use of hydrogen for expelling the air from the flasks before the sodium was heated, using the ammonia gas itself for that purpose.

Action with Potassic Benzolmonosulphonate. — One of the flasks containing the sodium amide was broken, its contents pulverized as rapidly as possible, and mixed (without separating the powdered glass from the flask) with anhydrous potassic benzolmonosulphonate in about the proportion of one molecule of each, calculated from the amount of sodium used in making the amide. The mixture was then heated gently over the lamp in a test-tube until the brown fused spots, which appear at first, had spread throughout the entire mass; but the process should be stopped before these spots show signs of decomposition, as, if the heat is carried too high, the yield is not so large. During the heating some aniline vapor escapes, but the amount of this is so insignificant, that it is not worth while to carry on the process in a retort. The product was then carefully treated with water, and distilled with steam as long as anything passed over. The presence of aniline in the turbid distillate was determined by its smell, by the strong purple color which the distillate gave with a solution of bleaching-powder, and by the analysis of the chloride made by adding dilute hydrochloric acid to the distillate, filtering, and evaporating to dryness.

0.4966 gr. of the salt gave 0.554 gr. of argentic chloride.

	Calculated for $C_6H_5NH_3Cl$.	Found.
Chlorine	27.41	27.60

The yield varied a great deal, but was in the neighborhood of 10 per cent, rising once as high as 15 per cent of the theory. The portion of the distillate insoluble in dilute hydrochloric acid consisted of white scales, which, after repeated recrystallization from ligroine, melted between 53° and 54°, and gave an intense blue color with strong nitric acid. We therefore inferred that they consisted of diphenylamine, an inference confirmed by the analysis of the chloride prepared by the action of strong hydrochloric acid and alcohol on the substance, which gave the following result.

0.1334 gr. of the salt gave 0.0916 gr. of argentic chloride.

	Calculated for $(C_6H_5)_2NH_2Cl$.	Found.
Chlorine	17.27	16.97

The formation of diphenylamine by this reaction would seem to show that the sodium amide used by us was a mixture of $NaNH_2$ with Na_2NH, whereas Beilstein and Geuther proved that the formula of their sodium amide was $NaNH_2$. The explanation of this difference probably can be found in the fact that our amide still contained an excess of sodium, the flasks used by us not being made of a sufficiently resistant glass to allow us to carry the reaction to an end, while in their experiments all the sodium was converted into the amide. It is also possible, but not probable, that the diphenylamine was formed by a secondary reaction from the aniline.

Some experiments to determine the temperature at which the reaction takes place showed that some amine was obtained at 280°, and the yield was not improved at 300–350°; but that a much better result was reached by heating over the free lamp than with an oil- or air-bath, the products at the temperatures given above amounting respectively to 6.8 and 5.4 per cent of the theoretical, or about one half of the amount obtained by the more rapid direct heating over the lamp.

Action with Potassic Benzolmetadisulphonate. — The salt mixed with about the equivalent amount of sodium amide was heated in a test-tube as before; but it was found necessary in this case to continue the heating until the brown spots which formed at first had turned black, and showed signs of decomposition, since, if the action was stopped while they were still brown, as in the case of the monosulphonate, the yield was exceedingly small. At best, the yield was not satisfactory, reaching at the outside five per cent of the theory, so that we did not attempt to collect enough of the tolerably unstable chloride of the metaphenylenediamine for analysis, but contented ourselves with proving its presence by qualitative tests. For this purpose, the product of the reaction was cautiously treated with water, and the aqueous solution extracted with ether; one portion of the ether extract was shaken with dilute sulphuric acid, and to the acid solution thus obtained a very minute amount of sodic nitrite was added, which turned it yellow; another portion of the ether extract was shaken with dilute hydrochloric acid, the acid solution evaporated to dryness, and the residue redissolved in water, filtered from brown decomposition products, and treated with a solution of sodic nitrite, when a heavy reddish brown precipitate of phenylene brown was formed; finally, another portion of the ethereal solution of the base was treated with a solution of the nitrate of diazobenzol, when a red crystalline precipitate was formed, which turned yellow upon the addition of ammonic hydrate, and was therefore the nitrate of chrysoidine. All these tests indicate the presence of metaphenylenediamine in the product of the action of sodium amide upon the potassic benzolmetadisulphonate. The small yield is undoubtedly due to decomposition of a portion of the diamine at the comparatively high temperature necessary for the reaction, as there was a large amount of tarry matter always associated with the product.